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NOTIFICATION OF ELECTION

(PCT Rule 61.2)

To:

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in its capacity as elected Office

Date of mailing: 21 October 1999 (21.10.99)	
International application No.: PCT/KR99/00142	Applicant's or agent's file reference:
International filing date: 26 March 1999 (26.03.99)	Priority date: 26 March 1998 (26.03.98)
Applicant: OH, Sea, Wha et al	

1. The designated Office is hereby notified of its election made:

[X] in the demand filed with the International preliminary Examining Authority on:

14 September 1999 (14.09.99)

[ ] in a notice effecting later election filed with the International Bureau on:

2. The election [X] was

[ ] was not

made before the expiration of 19 months from the priority date or, where Rule 32 applies, within the time limit under Rule 32.2(b).

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INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference	FOR FURTHER ACTION See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)	
International application No. PCT/KR 99/00142	International filing date (*day/month/year*) 26 March 1999 (26.03.99)	Priority Date (*day/month/year*) 26 March 1998 (26.03.98)
International Patent Classification (IPC) or national classification and IPC IPC[6]: C 09 B 62/51		
Applicant KOREA RESEARCH INSTITUTE OF CHEMICAL TECHNOLOGY et al.		

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TC 1700

1. This international preliminary examination report has been prepared by this International Preliminary Examination Authority and is transmitted to the applicant according to Article 36.

2. This REPORT consists of a total of 3 sheets, including this cover sheet.

☐ This report is also accompanied by ANNEXES, i.e., sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

These annexes consist of a total of _____ sheets.

3. This report contains indications relating to the following items:

- I ☒ Basis of the report
- II ☐ Priority
- III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- IV ☐ Lack of unity of invention
- V ☒ Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- VI ☐ Certain documents cited
- VII ☐ Certain defects in the international application
- VIII ☐ Certain observations on the international application

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Date of submission of the demand	Date of completion of this report
14 September 1999 (14.09.00)	27 June 2000 (27.06.00)
Name and mailing address of the IPEA/AT Austrian Patent Office Kohlmarkt 8-10 A-1014 Vienna Facsimile No. 1/53424/200	Authorized officer Hauswirth Telephone No. 1/53424/136

Form PCT/IPEA/409 (cover sheet) (July 1998)

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No.
PCT/KR 99/00142

I. Basis of the report

1. With regard to the **elements** of the international application:*

☒ the international application as originally filed

☐ the description:
pages _____, as originally filed
pages _____, filed with the demand
pages _____, filed with the letter of _____.

☐ the claims:
pages _____, as originally filed
pages _____, as amended (together with any statement) under Article 19
pages _____, filed with the demand
pages _____, filed with the letter of _____.

☐ the drawings:
pages _____, as originally filed
pages _____, filed with the demand
pages _____, filed with the letter of _____.

☐ the sequence listing part of the description:
pages _____, as originally filed
pages _____, filed with the demand
pages _____, filed with the letter of _____.

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.
These elements were available or furnished to this Authority in the following language _____ which is:

☐ the language of a translation furnished for the purposes of international search (under Rule 23.1(b)).

☐ the language of publication of the international application (under Rule 48.3(b)).

☐ the language of the translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

☐ contained in the international application in written form.

☐ filed together with the international application in computer readable form.

☐ furnished subsequently to this Authority in written form.

☐ furnished subsequently to this Authority in computer readable form.

☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.

☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. ☐ The amendments have resulted in the cancellation of:

☐ the description, pages _____.

☐ the claims, Nos. _____.

☐ the drawings, sheets/fig _____.

5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed, as indicated in the Supplemental Box (Rule 70.2(c)).**

** Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as „originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17).*

*** Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.*

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No.
PCT/KR 99/00142

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Claims	1,2	YES
	Claims	-	NO
Inventive step (IS)	Claims	1,2	YES
	Claims	-	NO
Industrial applicability (IA)	Claims	1,2	YES
	Claims	-	NO

2. Citations and explanations (Rule 70.7)

This report has been drawn in consideration of the search report prepared by the Austrian Patent Office dated 30 April 1999 (30.04.99) and the claimed priority dated 26 March 1998 (26.03.98). The two documents cited in the search report give examples of the state of the art.
Thus the criteria for patentability of the subject matter of the present application, i.e. novelty, inventive step and industrial applicability are evident.

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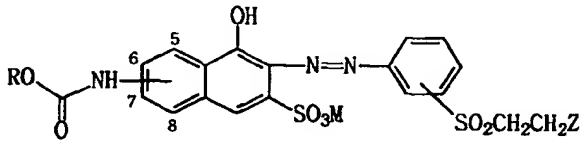
Published
With international search report.

(54) Title: REACTIVE ORANGE DYES CONTAINING VINYL SULFONES



(1)

(57) Abstract

The present invention relates to a reactive orange dye containing vinyl sulfone and more particularly, to the dye which have 6(7)- alkoxycarbonylamino-4-hydroxy-2-naphthalenesulfonic acid as a chromophore and aminophenyl-β-ethylsulfone derivative as an azo coupler. This dye provides excellent fastness in terms of light, washing, perspiration and chlorine as well as better dyeing yield than other monofunctional reactive dye. In Formula (1), M is alkaline metal atom; Z is $-O-SO_3M$ or $OC(O)CH_3$; R is alkyl group having 1-4 of carbon atom; and a position of C_6 or C_7 is substituted with carbamate group.

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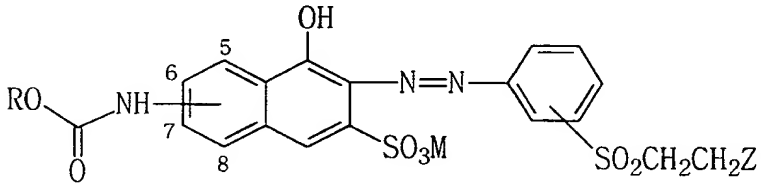
REACTIVE ORANGE DYES CONTAINING VINYL SULFONES

BACKGROUND OF THE INVENTION

Field of the Invention

The present invention relates to a reactive orange dye containing vinyl sulfone and more particularly, to the dye which have 6(7)-alkoxycarbonylamino-4-hydroxy-2-naphthalenesulfonic acid as a chromophore and aminophenyl-β-ethylsulfone derivative as an azo coupler. This dye provides excellent fastness in terms of light, washing, perspiration and chlorine as well as better dyeing yield than other monofunctional reactive dye:

Formula 1



wherein, M is alkaline metal atom; Z is $-O-SO_3M$ or $OC(O)CH_3$; R is alkyl group having 1-4 of carbon atom; and a position of C_6 or C_7 is substituted with carbamate group.

Description of the Related Art

In the case of using the conventional orange reactive dye containing a vinylsulfone-based compound for the manufacture of a black dye, a much larger amount of dye is needed in mixing for preparation of black dye. This is because the conventional orange reactive dye has lower several fastness, particularly, light fastness, and lower dyeing yield and the amount of wastefulness during washing is larger, which is responsible for the waste of dye, change of color and the difficulty of adjusting tone.

SUMMARY OF THE INVENTION

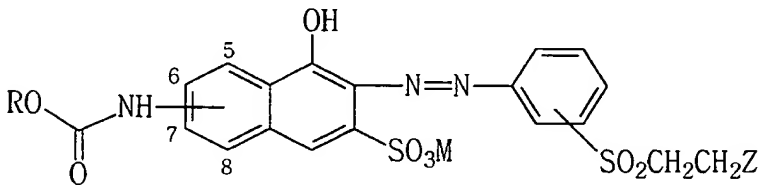
In an effort to solve the problems of conventional reactive orange dye containing vinyl sulfone, the inventors have made intensive studies and as a result they have developed the dye expressed in formula 1.

Accordingly, an object of this invention is to provide a reactive orange dye containing vinyl sulfone which has an excellent combination of properties such as better fastness in light, washing, perspiration and chlorine, superior dyeing yield compared to other monofunctional reactive dyes, and better effectiveness on dyeing of cellulose fibers for mixing color as well as single color.

Detailed Description of the Invention

This invention is characterized by a reactive orange dye containing vinyl sulfone expressed in the following formula 1:

Formula 1



wherein, M is alkaline metal atom; Z is $-O-SO_3M$ or $OC(O)CH_3$; R is alkyl group having 1-4 of carbon atom; and a position of C_6 or C_7 is substituted with carbamate group.

This invention is also characterized by a process for preparing a reactive orange dye containing vinyl sulfone expressed in the following formula 1, which comprises the steps of:

(a) diazotizing aminophenyl-β-ethylsulfone compound of formula 2;

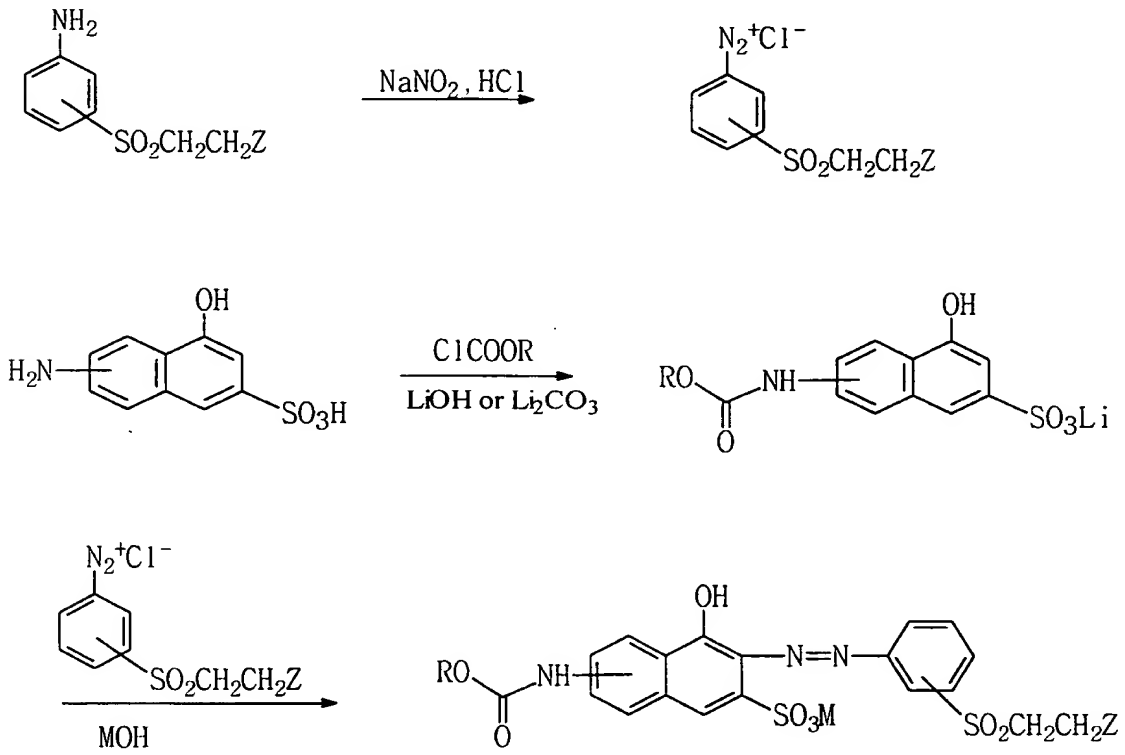
(b) condensing in such a manner that alkyl chloroformate is slowly added to neutralized solution of 6(7)-amino-4-hydroxy-2-naphthalenesulfonic acid to prepare 6(7)-alkoxycarbonylamino-4-hydroxy-2-naphthalenesulfonic

acid expressed in the following formula (3) at 0-25℃ with maintaining pH in the range of 3-6 by means of LiOH or Li_2CO_3; and

(c) coupling the reacting mixtures obtained in the above steps of (a) and (b) at 0-5℃ with adding a base so as to adjust pH lower than 6.5.

The process for preparing the reactive orange dye containing vinyl sulfone is expressed as the following Scheme1:

Scheme 1



(1)

wherein M is an alkaline metal atom; Z is $-OSO_3M$ or $OC(O)CH_3$; and R is alkyl group having 1-4 of carbon atom.

The first step is to diazonate 3(4)-aminophenyl-β-ethylsulfone. The diazotization is a commonly available method; 3(4)-aminophenyl-β-ethylsulfone is dispersed in water at 0-5°C, followed by the addition of concentrated hydrochloric acid and $NaNO_2$ to carry out diazotization reaction.

The second step is to generate a sulfonic acid lithium salt by

neutralizing 6(7)-alkoxycarbonylamino-4-hydroxy-2-naphthalenesulfonic acid with a base, preferably LiOH or Li_2CO_3. The amount of lithium base is determined by equivalent rate to the amount of 6(7)-amino-4-hydroxy-2-naphthalenesulfonic acid.

Then, with adjusting pH in the range of 3-6 by LiOH or Li_2CO_3, alkyl chloroformate is slowly added to the neutralized aqueous solution of 6(7)-alkoxycarbonylamino-4-hydroxy-2-naphthalenesulfonic acid lithium salt. In this reaction, it is necessary to use lithium base instead of NaOH, Na_2CO_3, KOH or K_2CO_3 which reacts with alkyl chloroformate to generate by-products. As a result of the above reaction, amine group of 6(7)-alkoxycarbonylamino-4-hydroxy-2-naphthalenesulfonic acid and alkyl chloroformate are condensed to give a 6(7)-alkoxycarbonylamino-4-hydroxy-2-naphthalenesulfonic acid expressed by following formula 3. An alkyl group of alkyl chloroformate is methyl, ethyl, n-propyl or n-butyl group. If the pH of condensation reacting solution is lower than 3, alkyl chloroformate becomes hydrolyzed; in the case of exceeding pH 6, it condensed with hydroxy group. Further, it is preferred that the condensation temperature is 0-25°C with addition of ice, more preferably 10-15°C. If the temperature is lower than 0°C, the reaction rate is extremely slow ; in the case of exceeding 25°C, the side reaction may occur.

The last step is to couple the diazo solution and condensing reaction mixture at 0-5℃ with adding a base so as to adjust pH in the range of 5- 6.5, finally preparing reactive orange dye containing vinyl sulfone expressed in the formula 1. If the pH is more than 6.5, reactive groups may be hydrolyzed.

The following specific examples are intended to be illustrative of the invention and should not be construed as limiting the scope of the invention as defined by appended claims.

Example 1

First, 8.44g(0.03mol) of 4-aminophenyl-β-sulfatoethylsulfone was dispersed in 70ml of water and after the dropping of $NaNO_2$ (10.5ml), the temperature was adjusted to 0-5℃, followed by the addition of ice (100g). Then, 6.52ml of 35% HCl was added to diazonate and excess of nitrous acid was removed with the addition of sulfamic acid.

60ml of H_2O was added to 7.18g (0.03mol) of 6-amino-4-hydroxy-2-naphthalene sulfonic acid and was then neutralized with 15ml of aqueous solution of 2N LiOH, after which pH was adjusted to 5.5-6.0 with 2N HCl, followed by the addition of 30g of ice. Thereafter, 3.58g (0.033mol) of ethyl chloroformate was slowly added to the reaction mixture in the presence of aqueous solution of LiOH for adjusting pH to be 3-6, which leads to condensation reaction. After the completion of the above reaction, salting-out and filtering was carried out following the adjustment of pH to 6.

Thereafter, the condensed solid of ethyl chloroformate is dissolved in 60ml of water and diazo solution was added for the purpose of coupling reaction at 0-5℃ with adjustment of pH to 5.0-6.5 by aqueous solution of Na_2CO_3. Following the completion of coupling reaction, spray-drying was performed and finally reactive orange dye containing vinyl sulfone (R=C_2H_5, Z=OSO_3Na) expressed in the formula (1) was prepared.

^{1}H-NMR(300 MHz, DMSO-d_6) : δ 1.26(3H, t), 3.63(2H, t), 3.96(2H, t), 4.16(2H, q), 7.49(1H, s), 7.66(1H, d), 7.80(1H, d), 7.90(2H, d), 7.96(2H, d), 8.41(1H, s), 10.06(1H, s), 15.50(1H, s)

Example 2

First, 7.30g(0.03mol) of 4-aminophenyl-β-acetoxyethylsulfone was dispersed in 70ml of water and after the dropping of $NaNO_2$ (10.5ml), the

temperature was adjusted to 0-5℃, followed by the addition of ice (100g). Then, 6.52ml of 35% HCl was added to diazonate and excess of nitrous acid was removed with the addition of sulfamic acid.

60ml of H_2O was added to 7.18g (0.03mol) of 6-amino-4-hydroxy-2-naphthalene sulfonic acid and was then neutralized with 15ml of aqueous solution of 2N LiOH, after which pH was adjusted to 5.5-6.0 with 2N HCl, followed by the addition of 30g of ice. Thereafter, 3.58g (0.033mol) of ethyl chloroformate was slowly added to the reaction mixture in the presence of aqueous solution of LiOH for adjusting pH to be 3-6, which leads to condensation reaction.

Thereafter, the diazo solution was added to the condensed solution of ethyl chloroformate and upon adjusting pH to be 5-6.5 with aqueous solution of Na_2CO_3, the coupling reaction was completed at 0-5℃. Finally, the resulting mixture was salting-outed and prepared reactive orange dye containing vinyl sulfone ($R=C_2H_5$, $Z=OCOCH_3$) expressed in the formula (1) was prepared.

^{1}H-NMR(300 MHz, DMSO-d_6) : δ 1.26(3H, t), 1.77(3H, s), 3.72(2H, t), 4.16(2H, q), 4.26(2H, t), 7.49(1H, s), 7.66(1H, d), 7.79(1H, d), 7.90(2H, d), 7.97(2H, d), 8.41(1H, s), 10.05(1H, s), 15.48(1H, s)

Example 3

First, 59.07g(0.21mol) of 4-aminophenyl-β-sulfatoethylsulfone was dispersed in 420ml of water and 43.5ml of 35% HCl was added at 0-5℃, followed by the addition of ice (100g). Then, 67ml of $NaNO_2$ was added to the reaction mixture for the purpose of diazolation, after which excess of nitrous acid was removed with the addition of sulfamic acid.

800ml of H_2O was added to 47.85g (0.2mol) of 7-amino-4-hydroxy-2-naphthalene sulfonic acid and was then neutralized with 40ml of aqueous

solution of 5N LiOH, followed by the addition of 150g of ice. Thereafter, 23.87g (0.22mol) of ethyl chloroformate was slowly added to the reaction mixture in the presence of aqueous solution of LiOH for adjusting pH to be 3-6, which leads to condensation reaction.

Then, the prepared diazo solution was added to the prepared ethyl chloroformate condensation solution and upon adjusting pH to be 5-6.5 with aqueous solution of NaOH, the coupling reaction was completed at 0-5℃. Finally, the resulting mixture was spray-dried and prepared reactive orange dye containing vinyl sulfone ($R=C_2H_5$, $Z=OSO_3Na$).

^{1}H-NMR(300 MHz, DMSO-d_6) : δ 1.26(3H, t), 3.63(2H, t), 3.95(2H, t), 4.17(2H, q), 7.40(1H, s), 7.61(1H, d), 7.75(1H, s), 7.88(2H, d), 7.92(2H, d), 8.15(1H, d), 10.24(1H, s), 15.56(1H, s)

Example 4

First, 12.17g(0.05mol) of 4-aminophenyl-β-acetosaethylsulfone was dispersed in 125ml of water and after the dropping of $NaNO_2$ (16.8ml), the temperature was adjusted to 0-5℃, followed by the addition of ice (30g). Then, 10.9ml of 35% HCl was added to diazonate and excess of nitrous acid was removed with the addition of sulfamic acid.

150ml of H_2O was added to 11.96g (0.05mol) of 7-amino-4-hydroxy-2-naphthalene sulfonic acid and was then neutralized with 10ml of aqueous solution of 5N LiOH, followed by the addition of 70g of ice. Thereafter, 5.97g (0.055mol) of ethyl chloroformate was slowly added to the reaction mixture in the presence of aqueous solution of LiOH for adjusting pH to be 3-6, which leads to condensation reaction.

Thereafter, the diazo solution was added to the condensed solution of ethyl chloroformate and upon adjusting pH to be 5-6.5 with aqueous solution

of NaOH, the coupling reaction was completed at 0-5℃. The resulting mixture was salting-outed and filtered, finally preparing reactive orange dye containing vinyl sulfone ($R=C_2H_5$, $Z=OCOCH_3$) expressed in the formula (1) was prepared.

^{1}H-NMR(300 MHz, DMSO-d_6) : δ 1.26(3H, t), 1.77(3H, s), 3.71(2H, t), 4.17(2H, q), 4.26(2H, t), 7.40(1H, s), 7.61(1H, d), 7.75(1H, d), 7.89(2H, d), 7.94(2H, d), 8.14(1H, d), 10.24(1H, s), 15.53(1H, s)

Example 5-20

The reactive orange dye containing vinyl sulfones represented in the following Table 1a-1b were prepared as in Example 1-4.

Table 1a

Category	Formula 2	R	Reactive group	Tone
Example 5	γ -acid*	CH_3	*p*-$SO_2CH_2CH_2OSO_3Na$	Redish orange
Example 6		C_2H_5	*m*-$SO_2CH_2CH_2OSO_3Na$	Redish orange
Example 7		C_3H_7	*p*-$SO_2CH_2CH_2OSO_3Na$	Redish orange
Example 8		n-C_4H_9	*p*-$SO_2CH_2CH_2OSO_3Na$	Redish orange
Example 9		CH_3	*p*-$SO_2CH_2CH_2OSO_3CH_3$	Redish orange
Example 10		C_2H_5	*m*-$SO_2CH_2CH_2OSO_3$ CH_3	Redish orange
Example 11		C_3H_7	*p*-$SO_2CH_2CH_2OSO_3CH_3$	Redish orange
Example 12		n-C_4H_9	*p*-$SO_2CH_2CH_2OSO_3CH_3$	Redish orange
Example 13	J-acid**	CH_3	*p*-$SO_2CH_2CH_2OSO_3Na$	Orange
Example 14		C_2H_5	*m*-$SO_2CH_2CH_2OSO_3Na$	Orange
Example 15		C_3H_7	*p*-$SO_2CH_2CH_2OSO_3Na$	Orange
Example 16		n-C_4H_9	*p*-$SO_2CH_2CH_2OSO_3Na$	Orange
Example 17		CH_3	*p*-$SO_2CH_2CH_2OSO_3CH_3$	Orange
Example 18		C_2H_5	*m*-$SO_2CH_2CH_2OSO_3$ CH_3	Orange

Table 1b

Category	Formula 2	R	Reactive group	Tone
Example 19	J-acid**	C_3H_7	*p*-$SO_2CH_2CH_2OSO_3CH_3$	Orange
Example 20		n-C_4H_9	*p*-$SO_2CH_2CH_2OSO_3CH_3$	Orange
* γ -acid: 6-amino-4-hydroxy-2-naphthalenesulfone acid **J-acid: 7-amoino-4-hydroxy-2-naphthalenesulfone acid				

Example 14

^{1}H-NMR(300 MHz, DMSO-d_6) : δ 1.26(3H, t), 3.66(2H, t), 3.98(2H, t), 4.18(2H, q), 7.33(1H, s), 7.47-7.68(2H, m), 7.65(1H, s), 7.74(1H, s), 8.19(1H, d), 8.21-8.68(2H, m), 10.06(1H, s)

Example 18

^{1}H-NMR(300 MHz, DMSO-d_6) : δ 1.26(3H, t), 1.75(3H, s), 3.77(2H, t), 4.18(2H, q), 4.29(2H, t), 7.39(1H, s), 7.63(1H, t), 7.68(1H, d), 7.71(1H, d), 7.76(1H, s), 8.16(1H, d), 8.18(1H, d), 8.19(1H, s), 10.23(1H, s), 15.69(1H, s)

Test

0. 02g (1.0% o.w.f. dyeing), 0.04g (2.0% o.w.f. dyeing) and 0.06g (3.0% o.w.f. dyeing) of the orange reactive dye prepared in the above was dissolved in 25ml of water, respectively and then 2g of cotton was added, followed by elevating temperature to 40℃. Then, 0.75g of sodium sulfate was added and the temperature is elevated to 60℃, followed by the addition of 0.75g of sodium carbonate. Dyeing is carried for 60 minutes and washed with cold water. The fabric is soaped off at 98℃ for 20 minutes, is rinsed once more and is dried. The dyeing yield and several fastness of the resulting dyed fabric were

measured.

In terms of dyeing yield, 1.0% o.w.f. dyeing shows 80-82% and 3.0% o.w.f. dyeing 82-84%, which is higher than monofunctional dye.

With respect to light fastness (KS K 0218 direct-illumination method), 1.0% o.w.f. dyeing shows 3-4th grade and 3.0% o.w.f. dyeing 4-5th grade.

Referring to the fastness on washing (KS K 030 A-4), perspiration (Acidity, Alkalinity; AATCC Method 14) and chlorine (JIS-0884-1983), this invention exhibits all 5th grade, which is excellent values.

Further, this invention shows excellent levelness of dyeing and reproducibility.

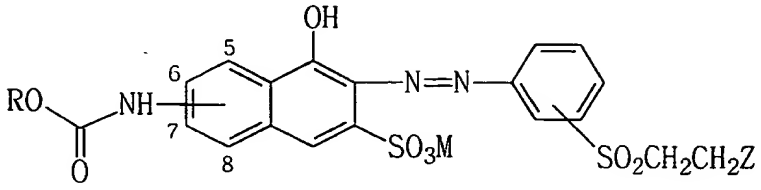
As described in the above, the reactive orange dye containing vinyl sulfone expressed in formula 1 shows excellent levelness of dyeing and reproducibility as well as several fastness, which is well applicable to dyeing of cellulose fabrics.

CLAIMS

What is claimed is:

1. A reactive orange dye containing vinyl sulfone expressed in the following formula 1:

Formula 1



wherein, M is alkaline metal atom; Z is $-O-SO_3M$ or $OC(O)CH_3$; R is alkyl group having 1-4 of carbon atom; and a position of C_6 or C_7 is substituted with carbamate group.

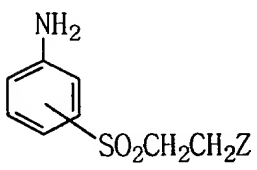
2. A process for preparing a reactive orange dye containing vinyl sulfone expressed in the following formula 1, which comprises the steps of:

(a) diazotizing aminophenyl-β-ethylsulfone compound of formula 2;

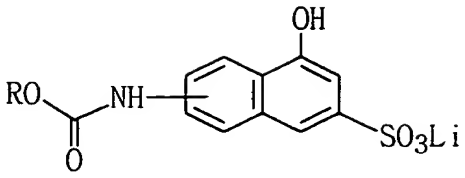
(b) condensing in such a manner that alkyl chloroformate is slowly added to neutralized solution of 6(7)-amino-4-hydroxy-2-naphthalenesulfonic acid to prepare 6(7)-alkoxycarbonylamino-4-hydroxy-2-naphthalenesulfonic acid expressed in the following formula (3) at 0-25℃ with maintaining pH in the range of 3-6 by means of LiOH or Li_2CO_3; and

(c) coupling the reacting mixtures obtained in the above steps of (a) and (b) at 0-5℃ with adding a base so as to adjust pH lower than 6.5.

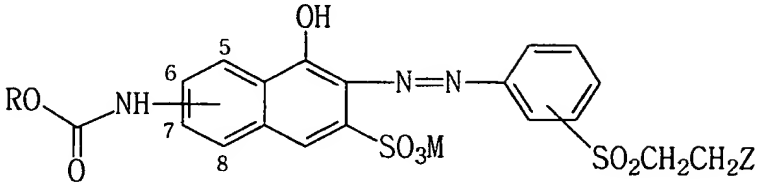
Formula 2



Formula 3



Formula 1



wherein, M is alkaline metal atom; Z is $-O-SO_3M$ or $OC(O)CH_3$; R is alkyl group having 1-4 of carbon atom; and a position of C_6 or C_7 is substituted with carbamate group.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/KR 99/00142

A. CLASSIFICATION OF SUBJECT MATTER

IPC[6]: C 09 B 62/51

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC[6]: C 09 B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	GB 1 289 159 A (FARBWERKE HOECHST AKTIENGESELL-SCHAFT) 13 September 1972 (13.09.72), claims 1,2,5,6; examples 1,6.	1,2
A	US 4 080 322 A (MISLIN et al.) 21 March 1978 (21.03.78), claims 1,29; column 4, lines 1-22.	1,2

☐ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

* Special categories of cited documents:
„A" document defining the general state of the art which is not considered to be of particular relevance
„E" earlier application or patent but published on or after the international filing date
„L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
„O" document referring to an oral disclosure, use, exhibition or other means
„P" document published prior to the international filing date but later than the priority date claimed

„T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
„X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
„Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
„&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
30 April 1999 (30.04.99)	29 June 1999 (29.06.99)

Name and mailing adress of the ISA/AT	Authorized officer
Austrian Patent Office Kohlmarkt 8-10; A-1014 Vienna Facsimile No. 1/53424/200	Hauswirth Telephone No. 1/53424/136

Form PCT/ISA/210 (second sheet) (July 1998)

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.
PCT/KR 99/00142

In Recherchenbericht angeführtes Patentdokument Patent document cited in search report Document de brevet cité dans le rapport de recherche	Datum der Veröffentlichung Publication date Date de publication	Mitglied(er) der Patentfamilie Patent family member(s) Membre(s) de la famille de brevets	Datum der Veröffentlichung Publication date Date de publication
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